Critical behavior of lead titanate near the ferroelectric phase transition

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A broad critical region has been observed in ferroelectric lead titanate by using an ESR method. This region exhibits a fluctuational broadening of the ESR line and a clearly defined transition to the classical behavior according to the Landau theory at lower temperatures.

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The only previous static observations of nonclassical critical behavior near antiferrodistortion and ferrodistortion second-order phase transitions have been in the electron-spin-resonance (ESR) measurements by Müller *et al.* in the perovskite crystals $SrTiO_3$ and $LaAlO_3$ (Ref. 1). The index $\beta = 0.5$ which corresponds to the Landau theory is seen in these materials far from T_c with a transition to the critical value $\beta = 0.33$ at $\epsilon = (T_c - T)/T_c < 0.1$. In this letter we are reporting the first observation of a broad critical region with $\epsilon \approx 0.1$ in the familiar ferroelectric $PbTiO_3$ near the ferroelectric transition ($T_c \approx 766$ K) from the tetragonal phase to the cubic phase. The anomalously prolonged critical behavior of the local crystal field in $PbTiO_3$ was observed by an ESR method involving impurity Fe^{3+} ions which replace Ti^{4+} ions in the crystal lattice. This behavior can be seen in the static properties (the index $\beta \approx 0.25$) and in the dynamic fluctuational broadening of the ESR line. the ESR measurements ($\lambda = 3$ cm) were carried out over the temperature interval 295–860 K with high-qua-

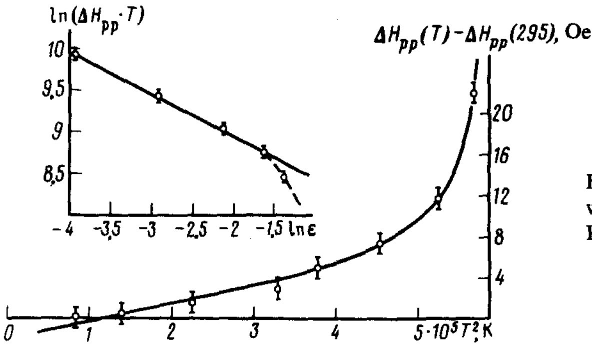

FIG. 1. Temperature dependence of the width of the ESR line of Fe^{3+} ions in $PbTiO_3$.

lity $PbTiO_3$ single crystals obtained from the $PbO–B_2O_3–TiO_2$ system.[2] The Fe^{3+} concentration $\sim 10^{19}$ cm^{-3} corresponds to a significant magnetic dilution, as was confirmed by experiments on the steady-state saturation of the Fe^{3+} ESR lines in $PbTiO_3$ and a study of the double electron-electron resonance in this system.[3] Under these circumstances we can estimate the temperature dependence of the electron spin-lattice relaxation rate, $T_{le}^{-1} \propto \Delta H_{pp}(T)$, far from T_c, and we can examine the critical dependence of the line width ΔH_{pp} near the transition point. Figure 1 shows linearized temperature dependences of the width of the Fe^{3+}ESR line in $PbTiO_3$ for the orientation of the external magnetic field H_0 orthogonal with respect to the [001] crystallographic direction. In the interval $295 < T < 580$ K, the dependence $\Delta H_{pp}(T) \propto T_{le}^{-1}$ corresponds to a two-phonon Raman process of spin-lattice relaxation. Near the phase transition ($\epsilon \lesssim 0.1$) the linear dependence of ln $(\Delta H_{pp} T)$ on lnϵ clearly demonstrates a broadening of the ESR line caused by fluctuations in the order parameter,[4] in this case fluctuations in the polarization and crystal field at the Ti^{4+} position. The polarization of the $\epsilon = 0.1$ region in $PbTiO_3$ is confirmed by the temperature dependence of the splitting factor in a zero field, D (Fig. 2), determined experimentally from the deviation of the effective g factor ($H_{0\perp}$[001]) from the value $g_\perp$ corresponding to Fe^{3+} ions in a strong, classical, axial field.[5] In the interval $0.4 < t < 0.9 (t = T/T_c)$ the $D(T)$ depen-

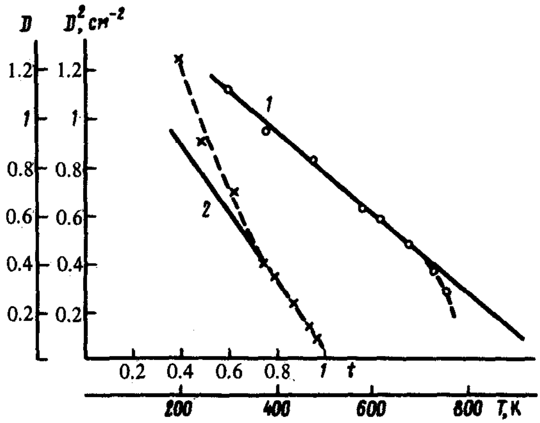

FIG. 2. Temperature dependence of the splitting factor in a zero field. 1—$D = D(T)$; 2—$D^2 = D^2(t)$.

dence corresponds to the Landau theory with $B \approx 0.5$, if we adopt $D = CP^2_S$, where P_S is the spontaneous polarization, which holds well in many studies.[6] At $t \gtrsim 0.9$ there is a significant deviation from the molecular-field approximation, and we have $\beta \approx 0.25$. This result is again at odds with the static critical dependence in $SrTiO_3$ and $LaAlO_3$, which corresponds to the three-dimensional Ising model with $\beta = 0.33$ and which is apparently a consequence of the nature of the first-order ferroelectric transition in $PbTiO_3$, for which the critical region can be expected[7] to be narrow. In $PbTiO_3$, nevertheless, the critical region has roughly the width as in impurity ferroelectrics which are isomorphic with lead titanate and which exhibit a "pure" second-order transition and underdamped soft modes: $SrTiO_3$ and $LaAlO_3$ (Ref. 1).

Lead titanate thus emerges as one of the first perovskite ferroelectrics in which well-developed critical phenomena exist in the scale of lattice-dynamics frequencies and static properties which are amenable to measurements by the ESR method.

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